

Contamination and Restoration of Groundwater Aquifers

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Humans are exposed to chemicals in contaminated groundwaters that are used as sources of drinking water. Chemicals contaminate groundwater resources as a result of waste disposal methods for toxic chemicals, overuse of agricultural chemicals, and leakage of chemicals into the subsurface from buried tanks used to hold fluid chemicals and fuels. In the process, both the solid portions of the subsurface and the groundwaters that flow through these porous structures have become contaminated. Restoring these aquifers and minimizing human exposure to the parent chemicals and their degradation products will require the identification of suitable biomarkers of human exposure; better understandings of how exposure can be related to disease outcome; better understandings of mechanisms of transport of pollutants in the heterogeneous structures of the subsurface; and field testing and evaluation of methods proposed to restore and cleanup contaminated aquifers. In this review, progress in these many different but related activities is presented.

Introduction

Figure 1 is a three-section diagram that presents the main processes that *a*) illustrate water transport in the atmosphere and subsurface (hydrologic cycle); *b*) identify activities and practices that cause contamination of groundwaters (groundwater contamination); and *c*) identify and illustrate proposed cleanup methods for contaminated aquifers (remediation). Terminology needed to understand groundwater contamination and remediation is introduced in Figure 1. The three-section diagram emphasizes that the transport of water and chemical contaminants in the subsurface occurs simultaneously. In this diagram, it can be seen that chemical contamination of groundwaters results in contamination of both the groundwater and the porous, solid matrix through which groundwater and contaminants flow, thus making remediation/restoration of the aquifer more difficult.

As seen by examining the hydrologic cycle section of Figure 1 in more detail, precipitation falling on land surfaces can either run off into surface waters or can infiltrate into the porous structure of the subsurface. In this way, ground and surface waters are connected. This linkage provides a direct conduit for entry of groundwater contaminants into surface waters and vice versa. Transport of moisture in the hydrologic cycle is driven by incident solar radiation.

In the subsurface, water is transported in aquifers. An unconfined or phreatic aquifer has a partially saturated zone, or unsaturated zone, above the water or saturated zone. The unsaturated zone of water-table aquifers has historically been where waste chemicals have been buried, where fuel and chemical storage tanks have been placed, and where agricultural chemicals (e.g., fertilizers, pesticides, herbicides) have been applied. Confined aquifers usually have low water permeability layers of

materials as upper and lower boundaries. Both types of aquifers are shown in Figure 1. The flow dynamics of each type of aquifer have many similarities but also many important differences that are important in developing remediation programs.

In the groundwater contamination section of Figure 1, chemical contaminants are transported by convection and dispersion through the porous matrix of the subsurface. Because of intermolecular forces between chemicals and the solid surfaces of the porous media, chemicals can bind to solid surfaces. The degree to which chemical contaminants are sorbed or bound to solid surfaces is a function of the chemical characteristics of both the chemical and the porous solid (substrate). Sorption usually has the effect of holding up or retarding transport. Chemical concentrations in groundwaters can be reduced either by abiotic or biotic mechanisms of degradation either in the liquid phase or in the sorbed phase. The rates of these processes occurring determine the quantities of these chemicals people are exposed to by drinking contaminated groundwaters.

To understand how contamination and exposure to toxic chemicals in groundwaters occurs and what will be necessary to reclaim or restore contaminated aquifers, mathematical models are required to determine the rates at which dissolved chemicals and nonaqueous phase liquids (NAPLs) are being transported and transformed in the subsurface. Exposure to toxic chemicals transported in the subsurface occurs by drinking contaminated groundwater and via inhalation of indoor air containing volatile chemicals that are transported in the subsurface and enter into homes through their substructures (e.g., basements, crawl spaces, cracks in slabs) (1).

Major sources of contaminants in groundwater resources are agricultural chemicals (2-4), leakage from underground storage tanks for liquid chemicals and fuels (5,6), chemical waste lagoons (7), subsurface disposal sites for chemical wastes, e.g., Superfund Waste Sites (8), low-level radioactive wastes (9), and

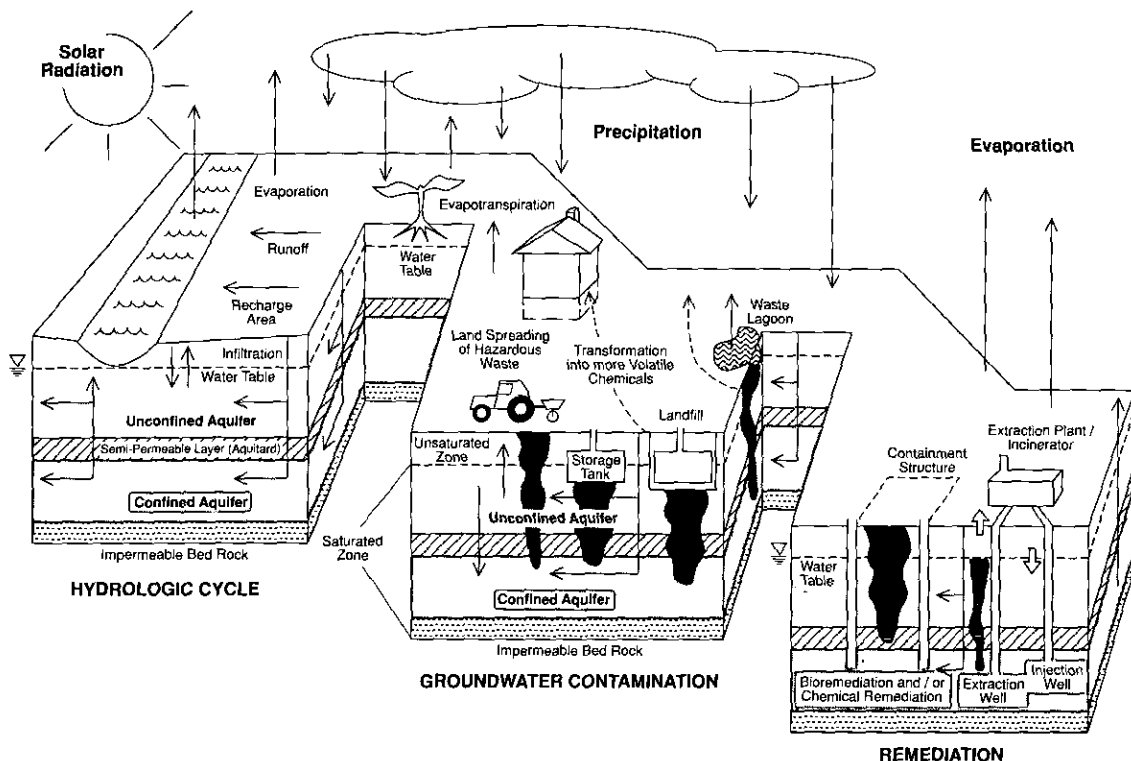


FIGURE 1. Contamination and restoration of polluted groundwater aquifers.

deep-well injection of toxic chemicals (10). Except for deep-well injection, all of these contaminating activities take place in the partially saturated region (unsaturated zone of unconfined aquifers) of the subsurface.

As a result of infiltrating moisture, usually from precipitation falling on the surface, chemicals are gradually transported by convection and dispersion downward into the saturated or groundwater zone of the subsurface. Chemicals that are soluble in water move with the aqueous phase. Their concentrations with space and time are functions of not only the velocity of the aqueous phase through the porous media of the subsurface, but also of dispersive, sorptive, and degradation processes that spread these chemicals out, retard their transport, and transform them into other chemicals. For NAPLs or chemicals such as gasoline or chlorinated solvents, transport in the subsurface is much more complex. In Figure 2, the density of the NAPL also plays an important role in subsurface transport. NAPLs that have densities less than water ride up or float on top of the groundwater phase. Volatile compounds of these NAPLs are transported surface via diffusion in the gas phase of the unsaturated zone. NAPLs that have densities greater than water gradually sink toward the lower confining boundary of the aquifer. Rates of transport of NAPLs in the subsurface are also functions of sorptive, dispersive, and transformation processes.

Restoration methods for contaminated aquifers are shown in the third section of Figure 1. These methods can be placed into two main categories: *in situ* and surface. The *in situ* methods are of two types. In the chemical *in situ* methods, chemicals are injected into the zone of contamination to mineralize pollutants (converting them into CO_2 and water). In the biological *in situ* methods, specially adapted microorganisms along with an adequate supply of nutrients are injected into the contaminant plume

to degrade pollutants. Surface remediation methods involve sinking extraction wells into the zones of pollution to remove contaminated groundwater. Conventional waste-water treatment technologies that use either chemical or biological methods or a combination of the two degrade pollutants in contaminated groundwater. Purified water is either consumed or reinjected into the subsurface. In another approach, toxic chemicals are first separated from contaminated groundwaters using methods such as sorption to activated charcoal or reverse osmosis. Chemicals separated in this manner can be biologically or chemically degraded or thermally degraded (incinerated).

The restoration of contaminated aquifers requires the coordinated efforts of many people who historically have not worked together. The researchers required to address the many problems associated with restoration of contaminated aquifers include investigators who study human health effects as a result of exposure to chemical contaminants in groundwaters; investigators who identify and validate the use of biomarkers of exposure; investigators who develop and test methods of describing and quantifying chemical transport in heterogeneous porous media; and investigators who develop and test methods of aquifer remediation. In this review, progress in these areas is presented.

Human Health Effects As a Result of Exposure to Groundwater Contaminants

Observed Human Health Effects Caused by Exposure to Agricultural Chemicals

The use of agricultural chemicals represents a major source of toxic chemicals in groundwaters. In identifying responses to

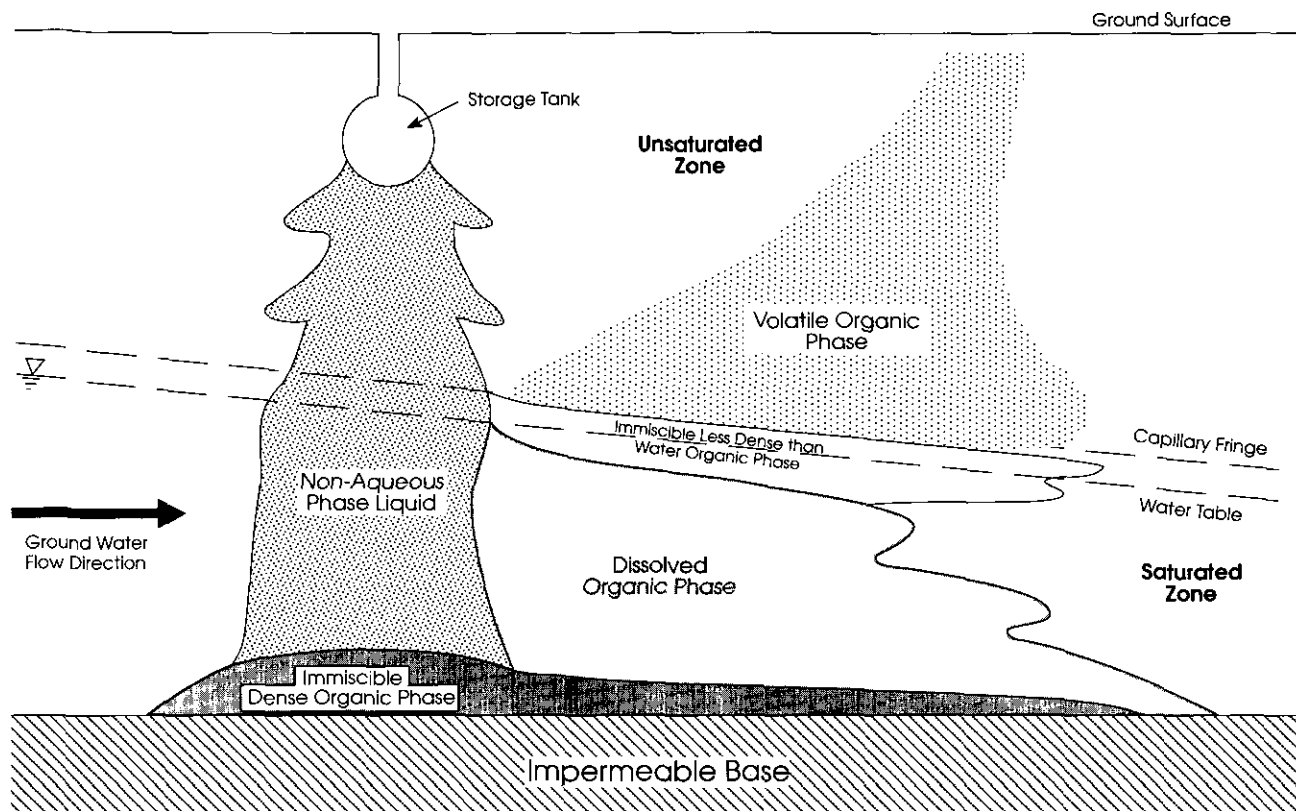


FIGURE 2. Transport of nonaqueous phase liquids in the subsurface. Adapted from Abriola (6).

toxic chemicals, agricultural workers and their families are important population groups to monitor because they are usually exposed to these chemicals in their jobs as applicators and sprayers to control weed and animal pests. Determination of toxic effects in this population as a result of exposure to the many different pesticide chemicals provides an important understanding of what to look for in populations drinking groundwaters contaminated with chemicals from this and other sources. It should be noted that exposures in these studies most likely occurred as a result of inhalation of sprays or by dermal contact.

Recently, a large number of both case-control and cancer incidence studies have shown that agricultural and forestry workers are at risk to contract leukemias (chronic lymphatic, acute lymphatic, and acute monocytic) and lymphoid neoplasms (non-Hodgkin's lymphoma, Hodgkin's disease, and multiple myeloma) (11-17).

For leukemias in agricultural workers in Nebraska, Blair and White (16) found the following relative risks (RR): chronic lymphatic, RR = 1.67; acute lymphatic, RR = 1.34; chronic lymphatic, RR = 1.94; and for acute unspecified, RR = 2.36. Most chronic lymphatic leukemias came from counties with large cattle and dairy operations. Most of the cases of acute lymphatic, acute monocytic, and acute unspecified leukemias came from counties with large corn production, hog and chicken raising, and heavy use of pesticides and fertilizers. In another case-control study in North Carolina, Dezell and Grufferman (18) found the RR for all leukemias in nonwhite farmers to be 1.9. Burmester et al. (19) carried out case-control studies for farmers

in Iowa who died between 1964 and 1978. For all types of leukemias, the RR = 1.24; for chronic lymphatic leukemia the RR = 1.70; and, for unspecified lymphatic leukemias, the RR = 1.66. Farmers in Iowa and Minnesota exposed to organophosphate pesticides have also shown a significantly elevated risk for leukemias (20).

Excess risk to farmers and forestry workers (especially herbicide applicators) for non-Hodgkin's lymphoma (NHL) has been reported for case-control studies in many countries worldwide and in many U.S. states with extensive farming activities. In Table 1, a summary of these studies is given (21-41). In one of the most extensive studies in the United States, Hoar et al. (34) found a significant relationship between exposure to chlorophenoxy herbicides, particularly 2,4-D, and risk of NHL. A 5- to 6-fold increased risk to NHL was seen in persons frequently exposed to chlorophenoxy herbicides (greater than 20 days/year) as compared with people with less than 20 days exposure/year and an RR of 8.0 for frequent exposures (greater than 40 days/year). In addition to an association with 2,4-D use, significant excesses in NHL were associated with use of triazine herbicides (e.g., atrazine, cyanazin, metribuzin, prometon, propazine, and terbutryn), amide herbicides (e.g., alachlor and propachlor), and the herbicide trifluralin (34).

Because the latency time for cancer to appear in a population is about 20 years after exposure occurred, and because the epidemiological studies reported for the United States have been recent, it is important to examine herbicide usage 20 years ago. In Figures 3 and 4, total herbicide use from 1966 to 1976 is shown,

Table 1. Epidemiological studies for non-Hodgkin's lymphoma by country and by state in the United States.

Country	Reference
Australia (Tasmania)	(21)
Canada (Saskatchewan)	(22)
Germany	(23)
Italy (northern)	(24)
New Zealand	(25-29)
Sweden	(30,31)
United Kingdom	(32)
United States	
Iowa	(33)
Kansas	(34)
Minnesota	(35)
Nebraska	(36-38)
Utah	(39)
Washington (western)	(40)
Wisconsin	(41)

along with amounts used on corn, soybeans, and wheat. The two main herbicides used for these crops were 2,4-D and atrazine (42,43)). In this 10-year period, 2,4-D use remained relatively constant at approximately 40 million pounds, whereas atrazine use rose from 23.5 million pounds in 1966 to 94 million pounds in 1976. By far the greatest use of herbicides during this 10-year period was in the production of corn, followed by soybeans and wheat.

In western Washington, Woods et al. (40) found a RR of 4.8 for forestry herbicide applicators, whereas the RR for all agricultural and forestry workers was 1.33. A study in Saskatchewan examined almost 70,000 male farmers and found that there was a significant dose-response relationship between risk of non-Hodgkin's lymphoma and number of acres sprayed in 1970 with herbicides (22). All of the studies cited above produced the same conclusion that the risk of NHL was significantly higher for male farm workers engaged in spraying chlorophenoxy herbicides. Finally, in a study in the districts of

Scarborough, York, and Leeds in England, Barnes et al. (32) found a greater incidence rate for NHL among rural residents than among urban residents.

For other lymphoid neoplasms associated with agricultural workers, Cuzick and De Stavola (44) reported an RR of 1.8 for multiple myeloma (MM) for agricultural/food processing workers in England and Wales. The authors found that the risk could not be restricted to those who came in contact with animals and meat products or those exposed only to pesticides. Significant excesses were also noted for people exposed to chemicals and gases/fumes, but no specific chemical or group of chemicals could be identified. For agricultural workers in northern Italy, La Vecchia et al. (24) found an RR of 2.0 for MM and 2.1 for Hodgkin's disease. In New Zealand, Pearce et al. (26) found an RR of 2.22 for MM in agricultural and forestry workers. For farmers in Iowa, Burmeister (33) reported an RR of 1.48 for MM.

Other toxic effects associated with occupational exposure to pesticides are delayed and progressive polyneuropathy from organophosphates (organophosphate-induced delayed neurotoxicity) (45,46) and delayed neurotoxicity as a result of ingestion of carbamate pesticides (47).

Human Health and Exposure to Toxic Chemicals in Groundwaters

Along with these epidemiological studies on farm workers and cancer incidence, other recent epidemiological studies have also reported higher cancer incidence rates for NHL in farm families in farming counties in eastern Nebraska (48) and have reported congenital cardiac malformations in newborn children near Tucson, Arizona (49,50). In these two Arizona studies, exposures to toxic chemicals occurred by ingestion of contaminated groundwaters. In the Nebraska study, higher incidences of NHL have been associated with extensive contamination of well water with

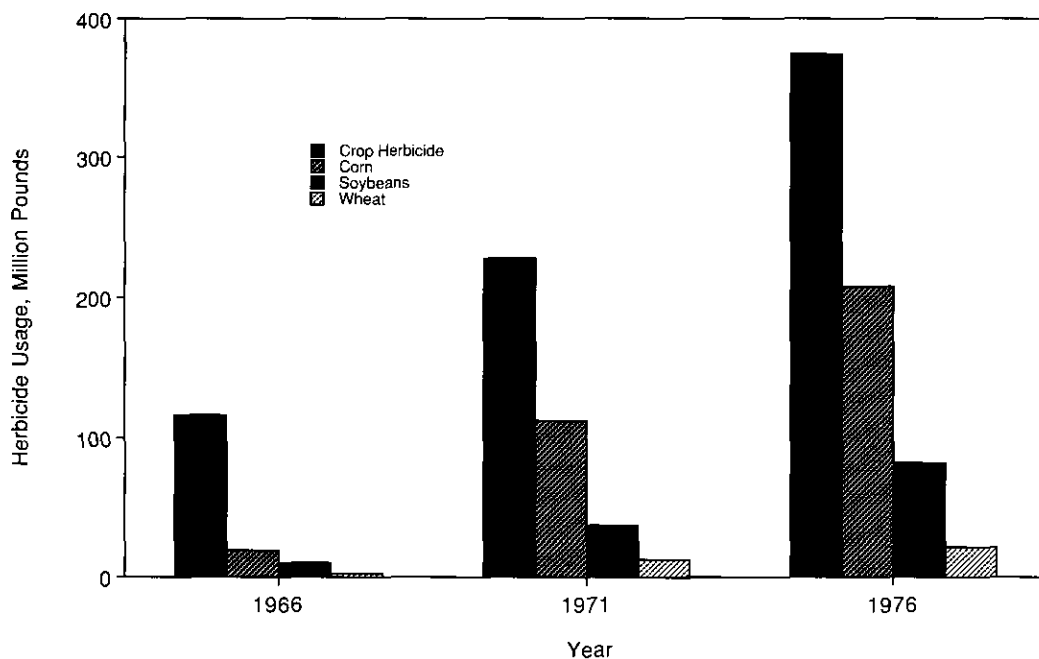


FIGURE 3. Herbicide usage from 1966 to 1976 with amounts used in various crops.

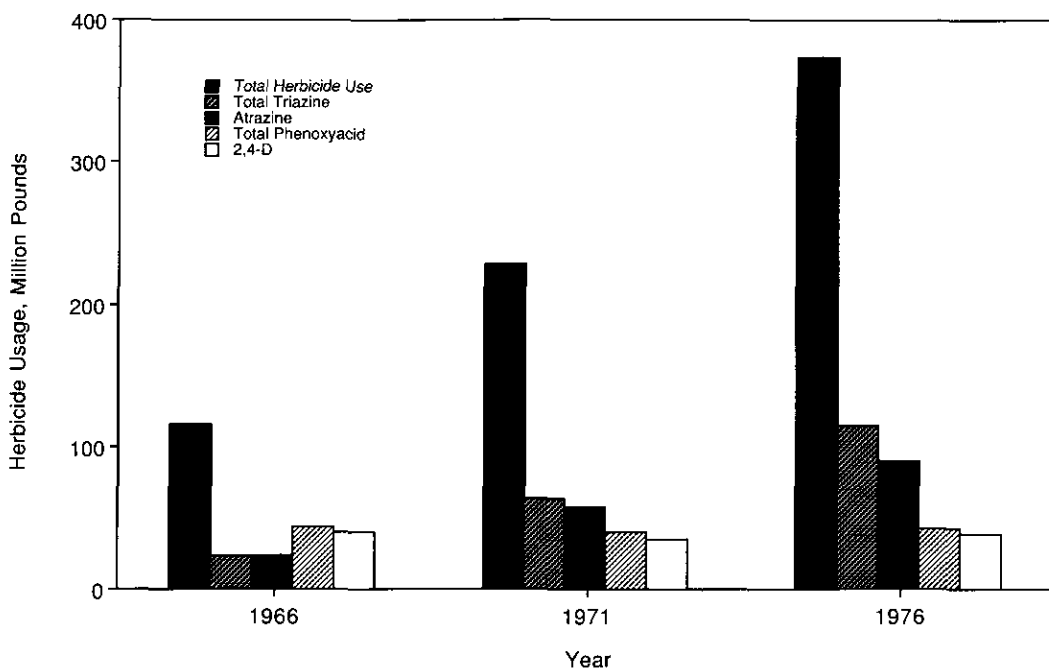


FIGURE 4. Herbicide usage from 1966 to 1976 for triazines and phenoxyacids.

nitrate and atrazine (48). Excess nitrate is added to corn, wheat, and soybean crops to improve yields, but the unused nitrate migrates into underlying groundwaters. In laboratory studies, *N*-nitrosoatrazine was formed from atrazine and nitrite (an *in vivo* reduction product of nitrates) at acid pHs characteristic of the stomach (51). This *N*-nitroso compound was found to be a weak mutagen in the *Salmonella* assay but strongly mutagenic in the Chinese hamster V-79 assay, producing revertants 3.4 times the dimethylnitrosamine control (52). Exposure to high levels of nitrates in drinking water has been linked with methemoglobinemia, especially in newborn children (53), but there are conflicting epidemiological study results on ingestion of nitrates and linkage to gastric cancer in adults (54). Congenital cardiac diseases (children with atrial tachycardia or premature infants with patent ductus arteriosus) in the Tucson Valley in Arizona have been associated with maternal ingestion of groundwaters contaminated with trichloroethylene (TCE) and to a lesser extent with dichloroethylene (49).

Laboratory animal studies have been used to examine the toxic effects of multiple chemical exposures to chemicals found in groundwaters (50,55). A mixture of trichloroethylene and dichloroethylene administered to a developing rat fetus *in utero* during the period of organ differentiation and development produced a greater number of cardiac defects in newborns than in control animals (50). In another experiment, mice were treated with a mixture of many common aliphatic and aromatic solvents and chlorinated solvents found in contaminated groundwaters near waste disposal sites plus arsenic, cadmium, chromium, lead, mercury, and nickel. After 108 days of exposure via drinking water, the mice showed suppressed marrow granulocyte macrophage progenitors (55), an indicator of immunosuppression.

Exposure to Toxic Chemicals and Biological Markers of Exposure

Adducts formed by reaction of nucleophilic amino acids found in biological macromolecules and genotoxic chemical species (e.g., parent chemicals, metabolites) are indicators of somatic mutation damage. Assays that quantify adduct formation may represent important indicators of human dosimetry by chemicals found in contaminated groundwaters (56–58). These biological markers of exposure may make it possible to link exposures to genotoxic chemicals to cancer outcomes in humans (59). The steps in the transformation of normal cells into neoplastic cells and their link to somatic mutations caused by activated chemicals have been studied extensively (60–62). Our understanding of these many processes has been improved, but there is still much that is unknown. In addition, there is accumulating evidence to suggest that adduct formation in many biological tissues and macromolecules may be linked to other disease outcomes as well. An example are the *N*⁷-guanyl adducts formed with 1,2-dibromo-3-chloropropane that have been linked with renal necrosis and testicular atrophy in laboratory animals (63). Adduct formation and the detection and quantification of adduct formation in human blood samples represents an important ongoing research program for linking chemical exposure to groundwater contaminants with disease outcome.

Chemical Transport in Heterogenous, Porous Media

Chemical Transport Processes in the Subsurface

Transport of chemicals in the subsurface involves transport of fluids and dissolved solutes through porous media. As a result, transport is a function of the properties of the chemical either

dissolved in the aqueous phase or in an NAPL and the chemical properties of the porous matrix through which the chemical is being transported. At any position and time within this porous structure, the concentration of chemical present is a function of four main processes: convection of the fluid phase as a result of pressure gradients in the aqueous/nonaqueous phase; dispersion as a result of gradients in fluid phase velocity and gradients in chemical concentration; abiotic and biotic reactions that degrade and transform the chemical both in the fluid phase and on the surfaces of the porous structure; and the strength of the sorptive processes that retard chemical transport. The concentration of a contaminant in either an aqueous or a nonaqueous phase at any given time and location is the sum total of these four processes.

For a porous media, aqueous-phase fluid transport through a porous media is described by Darcy's Law (64). The combined transport in porous media of aqueous and nonaqueous phase liquids is also described by Darcy's Law, but requires equations for each phase and an equation of state to describe interactions between phases (65,66). For organic pollutants, strong sorptive interactions greatly retard chemical transport in the aqueous/nonaqueous phase because the chemical is strongly held to the solid surfaces of the porous material, particularly the organic matter in the subsurface. In a like manner, weak sorptive interactions result in more rapid chemical transport in the subsurface. The degree of retardation can be estimated from the equilibrium sorption coefficient that describes the molecular interactions between the chemical and organic matter in soils (67,68). The rates of abiotic reactions are functions of the chemical properties of the chemical and the local temperature. Abiotic chemical reactions that occur most frequently for organic contaminants are hydrolysis and oxidation (69); however, it has been shown (70) that clay surfaces catalyze the formation of biphenyls and terphenyls from benzene. The rates of biotic reactions are a function of the microbial population present (71) and depth in the soil column. For a large number and variety of molecular structures of organic chemical contaminants, mechanisms of degradation mediated by microorganisms are usually oxidative, even for anaerobic conditions (72).

For a complete description of chemical transport in the subsurface, transport of heat and moisture must also be included. For the saturated zone of the subsurface, however, heat transfer is a minor consideration and for all practical purposes can be disregarded because transport is very nearly isothermal. In phreatic aquifers, particularly near the interface of the subsurface and the atmosphere, heat and moisture transport expressions are required. Chemical transport in the unsaturated zone occurs because of the simultaneous transport of chemical mass, moisture, and heat (73,74).

Modeling Chemical Transport in the Subsurface

To determine the amount of exposure that can occur, the changes in concentration as functions of time and distance from the source of contamination must be quantified. Frequently this is accomplished by translating a conceptual model that includes all the processes describing transport into a mathematical model that relates changes in concentration to changes in time and distance. Basically there are two ways to consider chemical transport in porous media, the eulerian and the lagrangian approaches. The eulerian approach defines a fixed region or

volume in the porous media and carries out a mass balance around this representative element of volume (REV). The lagrangian approach considers the meanderings of marked fluid particles moving with the aqueous phase. Both approaches are equally valid, but for our purposes we will concentrate on the eulerian approach. This approach illustrates the problems that must be overcome in developing reliable predictive mathematical tools to be used in remediation strategies for waste sites.

A generalized model describing moisture, heat, and chemical transport for both the unsaturated and saturated zones of the subsurface has been given by Piver and Lindstrom (74). The three mathematical equations describing transport are nonlinear, partial differential equations and represent the transport of a single chemical species in the subsurface. For multiple chemicals and transport of multiple liquid phases through the porous structure of the subsurface, the following modifications must be made: equations to describe transport of each phase; terms added to the chemical transport equations to describe interphase transport among the different phases (75); and additional equations to describe the transport in each phase of reactants and products of chemical reactions occurring by abiotic and biotic mechanisms. An example of the complexity of mathematical models needed to describe the transport for a single chemical contaminant in the unsaturated zone of the subsurface is given below.

The moisture transport equation is given as

$$\frac{\partial}{\partial t}(\rho_w \theta + \rho_{wv}^{\text{sat}}(T)h(\epsilon - \theta)) = -\nabla \cdot (\rho_w q V_w + \rho_{wv}(\epsilon - \theta)V_v) + Q_{\text{inj}} - Q_{\text{ext}} \quad (1)$$

and the heat transport equation is given as

$$\begin{aligned} \frac{\partial}{\partial t} \{ ((1-\epsilon) \cdot c_{\text{solids}} \rho_{\text{solids}} \\ + c_{\text{air}}(\epsilon - \theta) \rho_{\text{air}} + c_w \theta \rho_w) T \} \\ = -\nabla \cdot ((1-\epsilon)H_{\text{ss}} + \theta H_{\text{sw}} + (\epsilon - \theta)H_{\text{sv}}) \\ + c_w T_{\text{watin}} Q_{\text{inj}} - c_w T Q_{\text{ext}} \end{aligned} \quad (2)$$

where ρ_w is fluid density in g/m^3 ; θ is moisture content (dimensionless); ϵ is soil porosity (dimensionless); $\rho_{wv}^{\text{sat}}(T)$ is the density of the fluid at saturation in g/m^3 ; h is relative humidity, (dimensionless); V_w and V_v are the velocity vectors for the fluid in the liquid and vapor phases in cm/h ; ρ_{wv} is the density of the fluid in the vapor phase in g/m^3 ; c_{solids} , c_{air} , and c_w are the heat capacities of the porous matrix, air, and fluid phase, respectively in $\text{cal/g}^\circ\text{K}$; ρ_{solids} and ρ_{air} are the densities of porous solids and air respectively, in g/m^3 ; H_{ss} , H_{sl} , and H_{sv} are heat flux vector describing heat conduction through solids, heat conduction and convection in the liquid phase, heat conduction in the vapor phase, and the transfer of latent heat, respectively, in cal/hr m^2 ; and T is temperature, $^\circ\text{K}$. The three heat flux vectors are given as

$$H_{\text{ss}} = -\lambda_{\text{solids}}(x,y,z) \cdot \nabla T \quad (3)$$

$$H_{\text{sw}} = -\lambda_w I \cdot \nabla T + c_w \rho_w V_w T \quad (4)$$

$$H_{\text{sv}} = \zeta D_{\text{atm}} \alpha_{\text{tot}} \cdot \nabla \rho_{wv} - \lambda_{\text{air}} I \cdot \nabla T \quad (5)$$

where λ_{solids} and λ_{air} are the heat conductivities of solids and air in cal/hr m °K; ζ is the latent heat of vaporization in cal/g; I is the identity tensor (dimensionless); D_{atm} is the diffusion coefficient for the vapor in the atmosphere in m²/hr; and, α_{tot} is the tortuosity factor of the porous media (dimensionless).

The chemical transport equation is given as

$$\begin{aligned} \frac{\partial}{\partial t} \left\{ (\theta + (\epsilon - \theta) H_c + (\rho_{\text{solids}} K_{\text{dw}} \frac{\theta(1-\epsilon)}{\epsilon} \right. \\ \left. + \frac{(\epsilon - \theta)(1-\epsilon)}{\epsilon} \rho_{\text{solids}} K_{\text{dv}} H_c) C_w \right\} \\ = - \nabla \cdot (\theta q_{\text{cw}} + (\epsilon - \theta) q_{\text{cv}}) + Q_{\text{SO}}^{\text{BS}} \\ + Q_{\text{inj}} C_{\text{SO}} - \theta \Lambda C_w - \frac{Q_{\text{ext}} C_w}{\rho_w} \end{aligned} \quad (6)$$

where K_{dw} and K_{dv} are the sorption coefficients for chemical sorbed to solid surfaces from the liquid and vapor phases, respectively, in m³/g; H_c is the Henry's Law constant (dimensionless); C_w is the chemical concentration in the liquid phases in g/m³; q_{cw} and q_{cv} are the chemical mass flux vectors describing dispersion and convection of the chemical in the liquid and vapor phases in g/hr m²; Λ is the reaction rate term for abiotic and biotic reactions, in hr⁻¹; and, the Q -terms in the three balance equations (Eqs. 1, 2 and 6) represent source and sink terms for liquid, chemical mass, and heat. The two chemical mass flux vectors are defined as

$$q_{\text{cw}} = - D_{\text{cw}} \cdot \nabla C_w + V_w C_w \quad (7)$$

$$q_{\text{cv}} = - D_{\text{cv}} \cdot \nabla C_w + V_v C_v \quad (8)$$

where D_{cw} and D_{cv} are the dispersion coefficients for the chemical in the liquid and vapor phase, respectively, in m²/hr; and C_v is the concentration in the vapor phase in g/m³.

To apply these equations to the saturated zone, let $\epsilon - \theta = 0$. When proper boundary conditions are adjoined to Equations 1, 2, and 6 and when these equations are solved simultaneously, they represent the simultaneous transport of moisture, heat, and chemical mass in the subsurface. Because these equations are nonlinear and coupled, closed-form solutions are virtually impossible to find, and the equations must be solved numerically. In the most commonly used approach, a problem domain is defined in the subsurface and then subdivided into a network of nodes. Then approximating algebraic equations are chosen for this finite-dimensional space (finite element or finite difference approximations). A numerical procedure (solution algorithm) is developed to solve this huge set of discrete equations (74). It should be apparent from examination of Equations 1, 2, and 6 that there are a large number of variables and coefficients needed to carry out these calculations. In many instances, numerical values for these variables and coefficients either are unavailable or do not apply to the situation that is being simulated.

Because of the heterogeneity of the porous media of the subsurface, transport variables and coefficients do not vary in a deterministic manner from location to location on any dimensional scale. In many instances, values and equations defining important transport variables and coefficients describing chemical transport in the subsurface have come from observations in laboratory columns that are usually constructed to be uniformly homogeneous in composition and pore structure. In

these experiments, transport in a representative element of volume (REV) of the column is used to simulate transport behavior in the field. There have been some notable successes in using this strategy (76), and some notable failures (77). Unfortunately, in field situations the failures outnumber the successes. For regional contamination of the subsurface, composition and pore structure vary considerably and are not deterministic (78-88). Because the development of remediation programs for contaminated groundwaters depends on realistic representations of transport in porous media, the heterogeneity of the subsurface must be incorporated into predictive mathematical equations. In field situations, these variables and coefficients appear to be better represented as random variables, and the defining equations are stochastic (78-88).

In principle, the switch from deterministic variables to random variables is not as difficult as it sounds. One is now solving the same set of equations (Eqs. 1, 2, and 6, or suitable alternatives) for expected values of the dependent variables (e.g., fluid velocity, temperature and chemical concentration). For equations that must be solved by numerical methods, the equations can still be represented by either a finite difference or finite element approximation, except that now, the equations are stochastic. It has been shown (79,80,82) that the expected values of these variables can be represented by their mean values. As a result, if the main transport properties are random variables and are defined by probability distribution functions, then an iterative process such as the Monte Carlo method can be used to select random values from appropriate probability distribution functions for these transport properties and calculate a large number of expected values of the dependent variables. Then these expected values compose a set of values of the dependent variable that can be analyzed statistically. This is the approach that has been used by Lee and Kitanidis (89) to determine optimal remediation strategies for waste sites. Other approaches that represent the heterogeneous structure of the subsurface and look promising in describing transport make use of fractal geometry (90,91). The major drawback to this approach as it now exists is that an enormous number of calculations must be carried out to reach a solution. Thus, the examination of transport and remediation methods for contaminated aquifers requires a large commitment of resources.

Aquifer Remediation/Restoration

Because each groundwater aquifer is unique, mineralization of organic contaminants by either abiotic or biotic mechanisms (e.g., complete conversion of the chemical to CO₂ and water) is a function of the spatial heterogeneity of subsurface properties such as pore structure, hydraulic conductivity, and micro-organism populations as well as carbon and energy sources (92). This information, along with laboratory studies of degradation, sorption, and transport (as described by hydraulic conductivity and chemical dispersion), must be incorporated into plans to design and engineer the proper conditions for restoration in the field. The two approaches described below have some steps in common, but differ because biomediation methods are much more amenable to *in situ* operations. If *in situ* biomediation methods can be successfully transferred from the laboratory to the field, they have a clear economic and environmental advantage over physical-chemical methods.

Physical-Chemical Methods

Physical-chemical methods of aquifer remediation/restoration usually include drilling a well into the contaminant plume to remove contaminated groundwater to the surface. Then a variety of separation methods are available such as air stripping, activated charcoal, and reverse osmosis to remove contaminants from groundwater aquifers (93,94). After separating contaminants from the aqueous phase, there is still the problem of disposal of toxic organic chemicals, a process usually accomplished by incineration. Recently, studies have been carried out with modified clays that have demonstrated the capacity to adsorb pollutant chemicals from groundwater and then act as catalytic surfaces to decompose sorbed chemicals (95). At the present time, this method has not been field tested. In the field, it is proposed to locate a pit upstream from the direction of groundwater flow. The pit would then be loaded with the modified clay and pollutant chemicals would be sorbed onto clay surfaces and degraded.

Bioremediation

In the subsurface, biological degradation occurs naturally. However, for some refractory chemicals such as organochlorine pesticides and some organochlorine solvents (e.g., trichloroethylene and tetrachloroethylene), the rates of degradation in many soil environments are slow. Because of this, these chemicals travel great distances from their point of entry without much attenuation in initial entry concentration (96). Bioremediation of contaminated aquifers include removal of contaminated groundwaters to the surface and treatment in a bioreactor and *in situ* treatment (97). Bioreactors located on the surface have the advantage that within these containments bacterial growth can be carefully controlled, and appropriate amounts of oxygen and nutrients (nitrogen, phosphorous and carbon sources) can be added to promote rapid decay to high rates of conversion. There are major drawbacks to this method. The high pumping cost for removal of contaminated groundwater from the subsurface makes the capital and operating costs unfavorable. Also, this method can not remove contaminants sorbed or embedded in the porous media of the subsurface. These residuals represent long-term releasing sources of groundwater pollutants.

Many laboratory studies have been carried out with microorganisms extracted from contaminated aquifers to determine their ability to degrade a wide variety of organic chemicals (98-113). At the present time, there have been only a limited number of studies that have transferred laboratory experiments to field situations. In one study, coal tar chemicals, many of which were polynuclear aromatic hydrocarbons (PAHs) were being mineralized *in situ* by microorganisms adapted to PAH wastes (92). In another study (114,115) biotransformation of chlorinated ethenes (trichloroethylene and tetrachloroethylene) was accomplished by stimulating the growth of indigenous methane-oxidizing bacteria (methanotrophs), which transformed these solvents by a co-metabolic process to stable nontoxic end products. Biotransformation was enhanced by injecting methane and oxygen-containing groundwater in alternating pulses into the zone of contamination in the subsurface. These field experiments have demonstrated that microbial transformations observed in the laboratory can be promoted *in situ* in the field when proper conditions are observed.

Conclusions

Restoration of contaminated groundwaters will require coordinated research activities in many areas. Below are listed research needs suggested.

Biomedical Research Opportunities. Research is needed on noncancer end points as a result of exposure to multiple chemicals found in contaminated groundwaters. More research is needed on reproductive, behavior, immunotoxic, and neurotoxic effects because many toxic chemicals found in groundwaters have produced these types of effects already.

Development and expanded use of sensitive biomarkers of exposure in epidemiological studies is needed. Biomarkers of exposure with a high degree of specificity are needed to detect and quantify the very low, chronic exposures to waste site chemicals.

Nonbiomedical Research Opportunities. Research is needed on understanding transport processes for aqueous phase chemicals and NAPLs in different zones of the subsurface. Such studies would include development of methods to estimate important transport properties such as fluid conductivities, dispersivities, degradation rate constants, and equilibrium sorption coefficients. Also, research is needed on sorption and degradation mechanisms for single and multiple chemicals.

Research is needed on better mathematical models to describe transport of dissolved chemicals and NAPLs in the subsurface that would account for the heterogeneity of the subsurface. More attention needs to be given to validation and adaptation of laboratory studies on transport and biotransformation of chemicals to field applications.

If incineration is being considered as a waste disposal option for pollutants extracted from contaminated groundwaters, research is needed not only to determine the destruction efficiency of incineration, but also to determine the identities and quantities of by-products of incineration found in exhaust emissions and solid residues.

Metals pose a difficult waste-management problem. Special research is required on the chemistry, hydrogeology, and microbiology of the transport and transformation of metals in the subsurface. Remediation efforts should examine methods to modify the chemical forms of metals, to make them less mobile or to retard/sequester them in the subsurface. Metals of greatest concern include mercury, lead, cadmium, chromium, nickel, and arsenic.

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